

PATENT SPECIFICATION

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- (21) Application No. 12943/73 (22) Filed 17 March 1973
(23) Complete Specification filed 26 Feb. 1974
(44) Complete Specification published 20 Oct. 1976
(51) INT. CL.² C08L 23/08//C09J 7/02
(C08L 23/08 61/02)
(52) Index at acceptance
C3P 11D6 4D3B1 4K7 7D1A 7K4 E2 PC13A PC13B PC20D1



ERRATA

SPECIFICATION NO 1452911

Page 2, line 107, *for Eva read EVA*

Page 3, line 28, *after weight. start new line, insert Di-n-heptyl phthalate: 2 parts by weight.*

Page 3, line 30, *delete whole line*

THE PATENT OFFICE
6 December 1976

Bas 32390/23

PATENTS ACT 1949

SPECIFICATION NO 1452911

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated 19 June 1980 this Specification has been amended under Section 14 in the following manner:—

Page 1, line 19, *delete in*

Page 1, line 20, *after provides insert a plasticized vinyl chloride polymer surface having upon it*

Page 3, lines 96, 103, 107, 111, 115, 119 and 122, *delete An insert A plasticized vinyl chloride polymer surface having upon it an*

Page 3, lines 92, 127 and 130, *after A insert plasticized vinyl chloride polymer surface having upon it a*

Page 4, line 5, *for 3 read 6*

Page 4, *delete lines 6 to 17 insert*

11. A plasticized vinyl chloride polymer surface having upon it an adhesive composition according to any of the preceding claims, in which the vinyl chloride polymer is a homopolymer.
 12. A plasticized vinyl chloride polymer surface having upon it an adhesive composition according to any of claims 1 to 10, in which the vinyl chloride polymer is a vinyl chloride/vinyl acetate copolymer.
 13. A plasticized vinyl chloride polymer surface according to any of the preceding claims which is that of a sheet.
 14. A plasticized vinyl chloride polymer surface according to any of claims 1 to 13 which is that of a tile.
- Page 4, lines 18 and 19, *delete 11, 12, 13 or*
Page 4, *after line 24 insert*
17. A method of bonding a plasticized vinyl chloride polymer surface to another surface comprising employing as an adhesive composition for producing the bond a permanent tack adhesive composition as defined in any of claims 1 to 10.
 18. A method according to Claim 17, in which the permanent tack adhesive composition is applied in the form of a melt.
 19. A plasticized vinyl chloride polymer surface bonded to another surface by the method according to Claim 17 or 18.

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- (72) Inventors ALEC ELWORTHY
 PETER NYE



(54) ADHESIVES

(71) We, DUNLOP LIMITED, a British Company of Dunlop House, Ryder Street, St. James's, London S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to adhesives, and particularly to the provision of "permanent tack" adhesive compositions to be applied to the back of a tile.

By "permanent tack" is meant that property of an adhesive which allows the adhesive to retain a major proportion of its properties of adhesion after application to a surface, e.g. the back of a tile, for a long period of time.

Thus, in one aspect the present invention provides a "permanent tack" adhesive composition (as hereinbefore defined) comprising an ethylene-vinyl acetate copolymer, a plasticizer, and a cyclic ketone resin.

The adhesives of the present invention are particularly intended for use on the back of a tile. For storage purposes, the adhesive layer on the tile is generally covered with a release layer of, for example, paper or plastics foil which can be peeled off the tile when required.

The adhesive may be applied to the tile by any conventional technique. For example, a layer of adhesive may be calendered or roller coated onto the reverse face of the tile or the adhesive may be applied by a "hot melt" extrusion technique.

Many "permanent tack" adhesive systems have been proposed previously. However, one serious disadvantage of most known systems is that of migration between the adhesive layer and its substrate. A particular example of such migration occurs where the substrate is a PVC based tile. The PVC tile contains, amongst other compounded ingredients, a plasticizer, e.g. a phthalate

ester. When an adhesive layer is formed on the tile, it has been found that plasticizer migration takes place, particularly from the tile into the adhesive layers. This change in plasticizer content can deleteriously affect the properties both of the tile and of the adhesive. We have found that the use of an adhesive composition of the present invention effectively reduces such migration.

The ethylene-vinyl acetate copolymer (hereinafter referred to as EVA) used in the present invention may be any of the conventionally available members of that copolymer family, e.g. those having an acetate content of up to 45% by weight, preferably 15 to 40% and especially 30 to 40% by weight. Mixtures of two or more EVA copolymers may be used with advantage to obtain optimum properties.

Examples of suitable EVA copolymers include:

- a) *I.C.I. EVA copolymer grade 40-50*
 acetate content 40%
 melt flow index 50

This is a very soft EVA copolymer with a high acetate content which contributes to the tackiness of the adhesive mixture.

- b) *VYNATHENE EY 902-30*
 Acetate content 40%
 melt flow index 9

This is a copolymer of high molecular weight which imparts good cohesive strength and toughness to the adhesive system. Preferably it should not be used as the sole copolymer component in a hot melt adhesive formulation since it may create "stringing" problems in the molten state and may detract from the tackiness of the adhesive at ambient temperatures. This copolymer is, therefore, preferably used as one constituent of a blend of EVA copolymers.

- c) *ULTRATHENE UE 639*
 Acetate content 30%
 melt flow index 120

This copolymer can be used as a means

of reducing the "stringing" tendency in the hot adhesive, although it does not impart the same physical strength to the adhesive composition as EY 902-30.

5 The words "ULTRATHENE" and "VYNATHENE" are Registered Trade Marks.

The plasticizer may be any of those conventionally used to plasticize polymer compositions. Preferred plasticizers include 10 dibutyl phthalate, diamyl phthalate, dialphanyl phthalate and especially di-n-heptyl phthalate. Dialphanyl phthalate is a mixture of phthalate esters derived from Alphanol, which is itself a mixture of aliphatic 15 alcohols having from 7 to 9 carbon atoms in each alkyl group. ("Alphanol" is a Registered Trade Mark). Another suitable plasticizer is Pliabrac 810, this being a mixture of phthalate esters of octyl and 20 decyl alcohols, supplied by Albright and Wilson Limited. (PLIABRAC is a Registered Trade Mark).

The cyclic ketone resin, in conjunction 25 with the plasticizer, provides the required tacky properties of the adhesive composition. Ketone resins are generally manufactured by condensation of cyclic ketones,

suitable commercially available cyclic ketone resins being those supplied under the 30 description MS2 and MC2 by LaPorte.

Both of these resins are manufactured from cyclic ketones, the main difference between them being the presence of hydroxyl groups in the molecular structure of the 35 resin MC2. Both resins will take up phthalate ester plasticizers to form permanently tacky mixtures, this being the basis of the adhesion afforded. However, such resin/phthalate mixtures as are formed 45 by MS2 and MC2 resins appear to have reduced substantially the ingress of further plasticizers compared with resin ester/phthalate mixtures (which are the basis of many conventional ad- 50 hesives of this type). Thus, although the specification is not intended to be limited by any particular theory, it is believed that the rate of migration of plasticizer from a PVC compound into a cyclic ketone/phthalate 55 based adhesive is comparatively low. Typical figures for the weight transfer of phthalate plasticizers at 40°C. from both flexible and stiff plasticized PVC sheet into comparable EVA/resin/phthalate ester adhesives are as 60 follows:—

Adhesive mixture: EVA Ultrathene UE 639 2 parts:

65 Resin 5 parts: dialphanyl phthalate
3 parts

70 Resin Type	Plasticizer migration at 40°C. from flexible PVC sheet after 2 weeks contact	Plasticizer migration at 40°C. from stiff PVC sheet after 2 weeks contact
Laporte MS2 resin	15.6 g/m ²	3.4 g/m ²
75 Laporte MC2 resin	8.9	2.4
Foral 105 resin ester	19.6	6.3
80 Piccolite Alpha 115	19.7	6.4

The Foral and Piccolite materials are conventionally used tackifiers for adhesive systems and are supplied by Hercules and Pennsylvania Industrial Chemical Corporation respectively. "Foral" and "Piccolite" 85 are Registered Trade Marks.

These measurements were made by weighing samples, each of 10 square centimetres area, of the PVC sheet materials, 90 coating the samples on one side with the adhesive and placing them in an oven at 40°C. "Control" samples (uncoated sheets) are also placed in the oven, any weight losses which are observed in these control 95 samples being subtracted from the weight loss of the samples treated with the adhesive. (The adhesive coating can be readily removed from the samples using a soft

pencil eraser prior to re-weighing). In this way, using a range of samples in contact 100 with the adhesive, and heating the samples for different periods of time, the extent of net migration may be determined.

An adhesive of the present invention can conveniently be prepared by fusing and 105 mixing the components in the order cyclic ketone resin, Eva, and plasticizer. The temperature of mixing should be above the fusion temperature of the resin and the EVA copolymer and may, for example, be 110 in the range 125 to 170°C., for example, about 150°C.

Suitable proportions of the three components of the adhesive system of this invention are, for example: 115

EVA 20 to 50% by weight
Cyclic ketone resin 30 to 50% by weight
plasticizer 20 to 40% by weight.

The invention is further illustrated in the following Examples.

Examples 1, 2 & 3 (below) represent adhesives which were formulated in order to obtain optimum physical properties: the object being to strike a balance between such properties as tackiness, cohesive strength, viscosity at melt temperatures, stringing, and capillary absorption of the adhesive into a wooden surface.

EXAMPLE 1

I.C.I. EVA copolymer grade 40-50: 2 parts by weight.

Vynathene EY 902-30 EVA: 2 parts by weight.

Laporte cyclic ketone resin MC2: 9 parts by weight

Di-n-heptyl phthalate: 4 parts by weight.

EXAMPLE 2

I.C.I. EVA copolymer grade 40-50: 1 part by weight.

Ultrathene UE 639 EVA: 1 part by weight.

Laporte cyclic ketone resin MC2: 4 parts by weight.

EXAMPLE 3

Di-n-heptyl phthalate: 2 parts by weight.

I.C.I. EVA copolymer grade 40-50: 2 parts by weight.

VYNATHENE EY 902-30 EVA. 2 parts by weight.

Laporte cyclic ketone resin MC2: 9 parts by weight.

Di-Alphanyl phthalate: 4 parts by weight.

In another aspect the invention provides a tile having a permanent tack adhesive layer on one surface, the adhesive comprising an ethylene-vinyl acetate copolymer, a plasticizer and a cyclic ketone resin.

For example, the tile may be based on a vinyl chloride copolymer formulation, and Examples 4, 5 and 6 (below) show three typical vinyl tile formulations.

Example 4 shows a formulation suitable for a vinyl asbestos type of tile and Examples 5 and 6 show formulations suitable for a printed surface type of vinyl tile.

EXAMPLE 4

Asbestos: 26 parts by weight.

Ground limestone and pigments: 44 parts by weight.

Vinyl chloride/vinyl acetate copolymer (11% acetate): 16 parts by weight.

Phthalate plasticizer: 6 parts by weight.

Chlorinated paraffin: 5 parts by weight.

Stabilizers, processing aids: 3 parts by weight.

These proportions may, of course, be varied over quite a wide range. For example, 10 to 30% asbestos, 20 to 60% limestone and pigments and a total of 25

to 60% of plasticizer, chlorinated paraffin, stabilizers and processing aids could be employed.

EXAMPLE 5

Whiting and pigments: 56 parts by weight. 70

PVC homopolymer: 22.5 parts by weight.

Phthalate plasticizer: 11.5 parts by weight.

Chlorinated paraffin: 6.5 parts by weight.

Stabilizers, processing aids: 3.0 parts by weight. 75

Again, these proportions can be varied quite widely. For example, 40 to 70% of whiting and pigments and a total of 30 to 60% of the other ingredients could be employed. 80

EXAMPLE 6

Whiting and pigments: 56 parts by weight.

PVC homopolymer: 22.5 parts by weight

Phthalate plasticizer: 17 parts by weight (other than Pliabrac 810) 85

Stabilizers, processing aids: 5 parts by weight

A tile of this formation would be suitable for use with the adhesive composition of Example 3. 90

WHAT WE CLAIM IS:—

1. A permanent-tack adhesive composition (as hereinbefore defined) comprising an ethylene-vinyl acetate copolymer, a plasticizer and a cyclic ketone resin. 95

2. An adhesive composition according to Claim 1, in which the amounts of ethylene-vinyl acetate copolymer, plasticizer and cyclic ketone resin present in the adhesive are in the ranges 20 to 50% by weight, 20 to 40% by weight, and 30 to 50% by weight respectively. 100

3. An adhesive composition according to Claim 1 or 2, in which the ethylene-vinyl acetate copolymer has an acetate content in the range 15 to 45% by weight. 105

4. An adhesive composition according to Claim 3, in which the ethylene-vinyl acetate copolymer has an acetate content in the range 30 to 40% by weight. 110

5. An adhesive composition according to any one of the preceding claims in which the plasticizer is a dialkyl ester of phthalic acid.

6. An adhesive composition according to Claim 5, in which each of the alkyl groups in the plasticizer contains from 7 to 9 carbon atoms. 115

7. An adhesive composition according to Claim 5 or 6 in which the plasticizer is di-n-heptyl phthalate. 120

8. An adhesive composition according to Claim 5, in which the plasticizer consists of a mixture of dialkyl esters of phthalic acid, each alkyl group containing from 7 to 9 carbon atoms. 125

9. A permanent-tack adhesive composition according to Claim 1, substantially as hereinbefore described.

10. A permanent-tack adhesive composition. 130

tion comprising an ethylene-vinyl acetate copolymer, a plasticizer, and a cyclic ketone resin, substantially as hereinbefore described, with reference to any one of 5 Examples 1 to 3.

11. A tile having on one surface a permanent-tack adhesive composition according to any one of the preceding claims.

12. A tile according to Claim 11, made 10 from a composition based on a vinyl chloride homopolymer.

13. A tile according to Claim 11, made from a composition based on a vinyl

chloride/vinyl acetate copolymer.

14. A tile according to Claim 12 or 13, 15 substantially as hereinbefore described, with reference to any one of Examples 4 to 6.

15. A tile according to Claim 11, 12, 13 or 14, in which the layer of permanent-tack adhesive composition is covered with a 20 removable protective layer.

16. A tile according to Claim 15, in which the removable protective layer is paper or plastics foil.

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Agent for the Applicants.